

TECHNICAL NOTE

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EXPERIMENTAL INVESTIGATION OF CHEMICAL REGENERATION
OF SURFACES IN SIMULATED THERMIONIC DIODES

By Helmut F. Butze and Arthur L. Smith

Lewis Research Center
Cleveland, Ohio

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SUMMARY

An investigation was conducted to determine the feasibility of combating the sublimation of emitter material in thermionic diodes by means of chemical reactions designed to transport the sublimed material from the collector back to the emitter. Tests were conducted in a system consisting of a tungsten emitter, a tungsten collector, and chlorine gas. A sapphire light pipe embedded in the collector was used to monitor the deposition and, subsequently, the removal of condensed tungsten from the collector surface. At emitter temperatures of about 2170° to 2550° K and collector temperatures of about 1460° to 1730° K, previously deposited tungsten was removed from the collector at partial pressures of chlorine of 10^{-4} Torr and greater. The experimental results were consistent with those obtained in analytical studies that suggested chemical transport reactions involving halogens as a possible mechanism for maintaining the structural integrity of emitter and collector surfaces.

INTRODUCTION

Because the sublimation of materials from surfaces is a severe problem in many devices operated at very high temperatures, considerable research effort has been expended on its solution. Such a problem is encountered in the operation of thermionic diodes, which, for efficient utilization, must be operated at very high emitter temperatures over extended periods of time. With the extremely close spacing between emitter and collector required in these devices, operation at emitter temperatures a few hundred degrees below the melting point could sublime enough material to short out the cell after only a few days.

One of the methods suggested for combating the loss of emitter material due to sublimation is regeneration of the emitter surface by means of chemical transport reactions. In such a process a suitable gaseous material, such as a halogen, is introduced into the space between the collector and the emitter. The reactant combines with the sublimed material to form one or more chemical compounds. If the chemical thermodynamics are favorable, these compounds migrate back toward the emitter and there, upon decomposing, redeposit the emitter material.

Langmuir (ref. 1) demonstrated the feasibility of chemical regeneration by introducing a small amount of chlorine gas into a bulb containing a tungsten

filament. Subsequently, several patents have been issued covering the use of halogen gases in incandescent lamps. The application of this principle to the regeneration of emitter surfaces in thermionic diodes has been investigated analytically for continuum flow (ref. 2) and for free-molecule flow (ref. 3). The utilization of chemical transport reactions in thermionic diodes with uranium carbide emitters has been considered (ref. 4), but no experimental data are available at the present time.

The theoretical analyses of references 2 and 3 indicate the conditions of pressure and temperature under which chemical transport will possibly combat sublimation and also present some thermodynamic limitations on the materials that might be used. This report presents the results of an experimental investigation designed primarily to check, in a relatively simple system, the practical utility of the theoretical studies reported in reference 3; no conclusions as to the effect of halogens on the electrical performance of a thermionic diode should be drawn. Tests were conducted with a simulated diode consisting of a tungsten emitter and a tungsten collector with gaseous chlorine as the reactant. Emitter temperatures ranged from about 2170° to 2550° K, while collector temperatures varied from about 1460° to 1730° K. The system pressure was reduced to 10^{-5} Torr or lower before chlorine introduction; chlorine partial pressures were adjusted in steps until reaction occurred.

APPARATUS AND PROCEDURE

Test Unit

The test unit employed in this investigation simulated a thermionic diode and was designed for a study of the rate of deposition of emitter material on the collector and subsequent back transport to the emitter by means of a sapphire light pipe embedded in the collector. Variations in light output of this sapphire light pipe (partly coated with tungsten) served as a measure of the amount of emitter material deposited on the collector.

The basic test unit consisted of a tungsten emitter and a tungsten collector spaced 2 millimeters apart (at room temperature) and mounted in a water-cooled stainless-steel chamber (fig. 1) that was pumped down to pressures of 10^{-5} Torr or lower. The emitter was heated by electron bombardment from an electron gun, while the collector was heated by radiation and conduction from the emitter surface. No effort was made to control the collector temperature independently. The emitter and the collector were supported between tungsten flanges as shown in figure 1; this design made possible the machining of parts from single-crystal stock and, in addition, minimized heat losses by conduction.

The emitter and its support flange divided the test chamber into two compartments, which were connected to a common pumping system. The upper compartment contained the electron-gun heater and was always open to the vacuum system. The lower compartment, which included the reaction chamber, could be isolated from the pumping system by means of a valve; thus, it was possible to set up quasi-static conditions during the reaction cycle. Gaseous chlorine was admitted to the lower chamber through a variable leak and flowed into the reaction

volume between the emitter and the collector through several passages (fig. 1). Rubber or Teflon O-rings were employed wherever probes were introduced into the vacuum chamber.

The emitter temperature was measured by sighting an optical pyrometer through a quartz window into a blackbody cavity machined into the emitter body. A movable shutter protected the window from contamination at all times, except during the brief intervals in which temperature measurements were made. The temperature gradient between the blackbody cavity and the emitter face was determined in a separate calibration in which an open-bead tungsten - tungsten-26-percent-rhenium thermocouple was inserted through the light-pipe hole in the collector and butted against the emitter face. All emitter temperatures given in this report were corrected for this gradient. The collector temperature was measured by a tantalum-sheathed platinum - platinum-rhodium thermocouple inserted into the collector to within 0.030 inch of the collector face.

The process of condensation of tungsten on the collector and of subsequent back transport to the emitter was monitored by means of a 0.062-inch-diameter sapphire light pipe, which fitted snugly through an axial hole in the collector so that the end of the rod was flush with the collector face. The other end of the light pipe was focused on a photocell - the output of which was measured with a sensitive millivoltmeter. A chemical analysis showed that the deposit on the end of the sapphire light pipe was tungsten. Microscopic examination of the end of the rod before and after coating showed definite changes in the appearance of the surface after coating; the appearance of the coated surface resembled that of the tungsten collector. From calculations of the evaporation rate of tungsten, it was estimated that after 30 hours of operation at an emitter temperature of 2300°K , at least an average of 20 monolayers of tungsten had been deposited over the entire surface. It is reasonable to assume that with deposits of that thickness the characteristics of the surface were similar to those of the bulk tungsten metal.

The pressure in the system prior to chlorine introduction was determined with an ion gage located in the manifold connecting the upper and lower chambers to the vacuum system. A photograph of the experimental unit is shown in figure 2.

Chlorine System

Gaseous chlorine was obtained from a pressurized cylinder and expanded into a system of glass vessels, where it was possible to control the pressure over a wide range. Pressures were determined with a specially calibrated Pirani gage located in the lower vacuum chamber. Earlier attempts to determine chlorine pressures from the decomposition pressures of platinous chlorides had been unsuccessful, because it was difficult to avoid temperature gradients in the furnace and, thus, to pinpoint the decomposition pressure.

In order to approach static conditions in the reaction volume, it was necessary to isolate the lower chamber from the vacuum system by means of a valve and to balance the leakage into the upper chamber by bleeding in chlorine gas through a controlled leak. This was accomplished by expanding the gas from the

cylinder into glass flasks and then through a porous-tungsten plug into the lower vacuum chamber. Thus, by regulating the pressure upstream of the tungsten plug, it was possible to achieve any desired partial pressure of chlorine in the chamber.

In the parts of the system exposed to chlorine gas, materials resistant to chlorine attack were used. All metal-to-glass connections were made with specially machined Teflon connections.

The glass system used both for calibration of the Pirani gage and for control of chlorine pressures during operation is shown schematically in figure 3. It consisted essentially of a set of accurately calibrated volumes that provided expansion ratios as high as 4000. The entire apparatus was first pumped down to pressures of 10^{-5} Torr or less and was then isolated from the pumping system by means of a stopcock. Chlorine was introduced into one of the small-volume flasks and its pressure measured with an absolute manometer and a cathetometer. A layer of a fluorocarbon-type protective fluid covered the surface of the mercury exposed to the chlorine. The gas trapped in the small flask was then expanded into the larger volume flask and a reading obtained on the Pirani gage connected to the large flask. Then, from the measured pressure before expansion and the known expansion ratio, the pressure after expansion could be calculated. A check on the method was obtained by calibrating the system with air and replacing the Pirani gage with a McLeod gage. During operation the Pirani gage was installed directly in the lower vacuum chamber, and the porous-tungsten plug was installed between the large flask and the lower vacuum chamber.

Repeated calibration checks showed that the Pirani gage was capable of measuring chlorine pressures accurately over a range from 1×10^{-3} to 200×10^{-3} Torr. The calibration curve presented in figure 4 shows that, for the range of pressures investigated, the calibration curves for air and chlorine practically coincided; thus, it was possible to check the calibration frequently with air only.

Operational Procedure

Prior to a test, the pressure in the test chamber was reduced to a value of 10^{-5} Torr or less. The emitter was then heated with the electron gun, and pertinent data, such as emitter and collector temperatures and light transmission of the sapphire rod, were recorded. This condition was maintained until sufficient tungsten condensation had taken place to reduce the light output to a small fraction of the initial value. This generally required at least 30 hours, depending on temperature. It was advantageous to operate at as high an emitter temperature as possible in order to reduce the time required for coating.

After the sapphire light pipe had been coated, the emitter temperature was adjusted to the desired value. The lower vacuum chamber was then isolated from the pumping system, and chlorine was introduced through the controlled leak. Light transmission and pressure readings were recorded every minute for a period of 10 minutes. If no significant change in light output occurred, the chlorine pressure was increased, and the test was repeated until a substantial increase in light output had been attained. The chlorine supply was then shut off, and the

lower chamber was again connected to the pumping system. When the pressure had been reduced to a value of 10^{-5} Torr or less, the emitter temperature was again raised until sufficient tungsten condensation had taken place for another test.

RESULTS AND DISCUSSION

As previously stated, the object of this investigation was to determine (1) whether mass transport reactions are effective at operating conditions and with surface geometries that might be encountered in thermionic diodes, and (2) whether the experimental data can be bracketed by the results of the analytical study reported in reference 3.

Condensation of tungsten on the collector surface, including the sapphire light pipe, occurred very slowly and depended on emitter temperature. A typical plot of the condensation process is shown in figure 5, where light output of the sapphire rod is plotted against time. In general, chlorine tests were not started until after the light transmission through the sapphire light pipe had been reduced to a value of 10 millivolts or less. Inasmuch as the light transmission through a given thickness of coating increased rapidly with increasing temperature, however, it was occasionally expedient to begin chlorine tests at a higher initial level of light output (see fig. 6(g)).

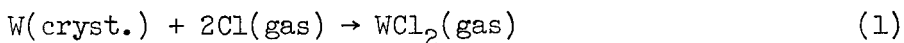
The results of the initial chlorine tests are shown in figure 6. The data are shown for four emitter temperatures, ranging from 2173° to 2548° K. Collector temperatures varied from 1472° to 1733° K. The plots show that mass transfer, as evidenced by increases in light output of the sapphire light pipe, occurred at partial pressures of chlorine of 5×10^{-3} Torr or greater. At an emitter temperature of 2173° K and a pressure of 1.8×10^{-3} Torr (fig. 6(a)), only a small increase in light output was noted in 10 minutes, while at a pressure of 5.2×10^{-3} Torr (fig. 6(b)), a substantial increase in light transmission was observed in the same time interval. Similar effects were noted at the higher temperatures.

The data presented in figure 6 give reasonably good evidence that the mass transport reactions take place in the pressure range 5×10^{-3} to 15×10^{-3} Torr and above; higher pressures generally increased the speed of the reaction, but correspondingly increased the time required to reduce the system pressure in preparation for a new test. No definite conclusions can be drawn, however, as to the low-pressure limits of the reaction. Inasmuch as small fluctuations in emitter temperatures can cause appreciable differences in light transmission, it was often difficult to know whether small changes in light output were the result of temperature fluctuations or of incipient mass transport reactions. Furthermore, chlorine pressures less than 2×10^{-3} Torr were difficult to adjust and to measure.

The data tended to indicate, however, that mass transport might occur at pressures below 1×10^{-3} Torr, although the rate of the reaction might be extremely slow. Accordingly, several tests were set up in which the partial pressure of chlorine was maintained, over a period of several hours, in the 10^{-4} Torr range, as estimated from an extrapolation of the volume expansion data. The results of these tests are presented in figure 7. At an emitter temperature of 2177° K and an estimated chlorine pressure of 0.4×10^{-3} Torr (fig. 7(a)), no

significant increase in light transmission was observed in 10 minutes; however, after 4 hours of operation, the light output had increased substantially, which indicated that mass transport reactions were occurring, although, from experimental considerations, the rate was extremely slow. Similarly, at an emitter temperature of 2464°K and a pressure of 2×10^{-3} Torr (fig. 7(b)), operation over several hours resulted in a substantial increase in light output.

In order to compare the experimental data with the values obtained in the analytical investigation, it is well to review the relations established in reference 3. The analysis was based on considerations of thermodynamic properties of materials and of mass transport phenomena in free-molecule flow. Equations were set up with the assumption of equilibration at the emitter and the collector surfaces and with departure from equilibration expressed by a single parameter called the recombination coefficient. Thus, a recombination coefficient of 1.0 indicated that the flux of particles from a given surface was dictated by equilibrium conditions, while a recombination coefficient of zero referred to a condition of no chemical reaction, that is, the case in which the flux of particles leaving a surface was the same as that arriving at that surface. The rate-controlling factor was assumed to be the rate of sublimation from the surface of the emitter. These considerations then led to a set of complex simultaneous equations that expressed the total pressure or particle concentration as a function of the recombination coefficient, the heat of vaporization of the metal, the equilibrium constant, and the heat of the reaction. A computer solution of a typical set of curves for the tungsten-chlorine (W-Cl) system, where the principal reaction is given by



is presented in figure 8 for a recombination coefficient of 1.0. The minimum pressure for reaction increases with increasing emitter temperature and with decreasing temperature difference between emitter and collector. When the temperature difference becomes zero, the expressions used to compute figure 8 can be simplified to yield the following equation:

$$P_{\text{Cl}} = K^{-1/2} \left[\frac{\left(\frac{2 - \gamma}{\gamma} \right) P_{\text{W}}}{\frac{-\Delta H_1}{\Delta H_V}} \right]^{1/2} \quad (2)$$

where

P_{Cl} partial pressure of chlorine

K equilibrium constant of reaction (1)

γ recombination coefficient

P_{W} saturation pressure of tungsten vapor

ΔH_1 heat of reaction (1)

ΔH_v heat of vaporization of tungsten

This expression leads to a simple criterion useful in screening materials for tests in regenerative cycles. This criterion is simply that reactions between surfaces to be regenerated and a reactant gas to form a gaseous product should be exothermic ($\Delta H < 0$).

A cross plot of values for the tungsten-chlorine system for recombination coefficients of 1.0, 0.1, and 0.01 at emitter temperatures of 2177° and 2464° K is presented in figure 9 along with experimental data obtained in this investigation. At an emitter temperature of 2177° K and a temperature difference between emitter and collector of 716° K, the experimental value suggested that the recombination coefficient was not smaller than about 0.02, while, at an emitter temperature of 2464° K and a temperature difference of 784° K, the experimental value approached a recombination coefficient of 1.0. Thus, it can be seen that there is reasonable agreement between analytically and experimentally determined values, especially since the experimental values must be considered as only a rough approach to limiting pressure conditions.

CONCLUDING REMARKS

In this investigation an attempt was made to study the regeneration of emitter surfaces in thermionic diodes through the introduction of halogen gases into a simulated diode.

The results obtained indicate that, for a system consisting of a tungsten emitter, a tungsten collector, and chlorine gas, mass transport reactions carrying previously deposited emitter material away from the collector occur at partial pressures of chlorine of 10^{-4} Torr and higher at emitter temperatures of approximately 2170° to 2550° K and collector temperatures of about 1460° to 1730° K. Furthermore, the results are in reasonable agreement with those of analytical studies (refs. 2 and 3) that suggested chemical transport reactions involving halogens and other gases as a possible mechanism for maintaining the structural integrity of emitter and collector surfaces.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, May 7, 1963

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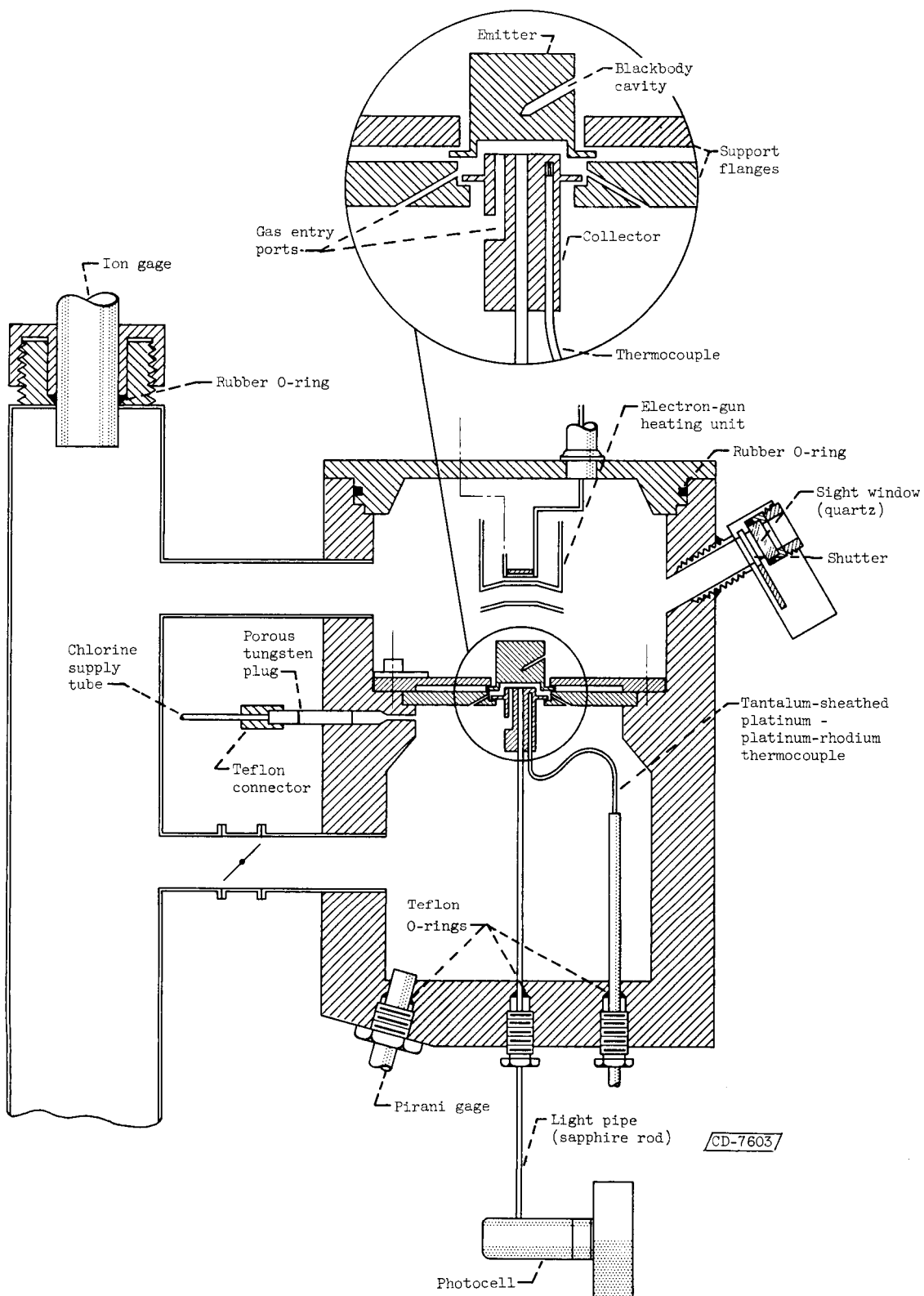


Figure 1. - Schematic drawing of simulated diode and auxiliary equipment.

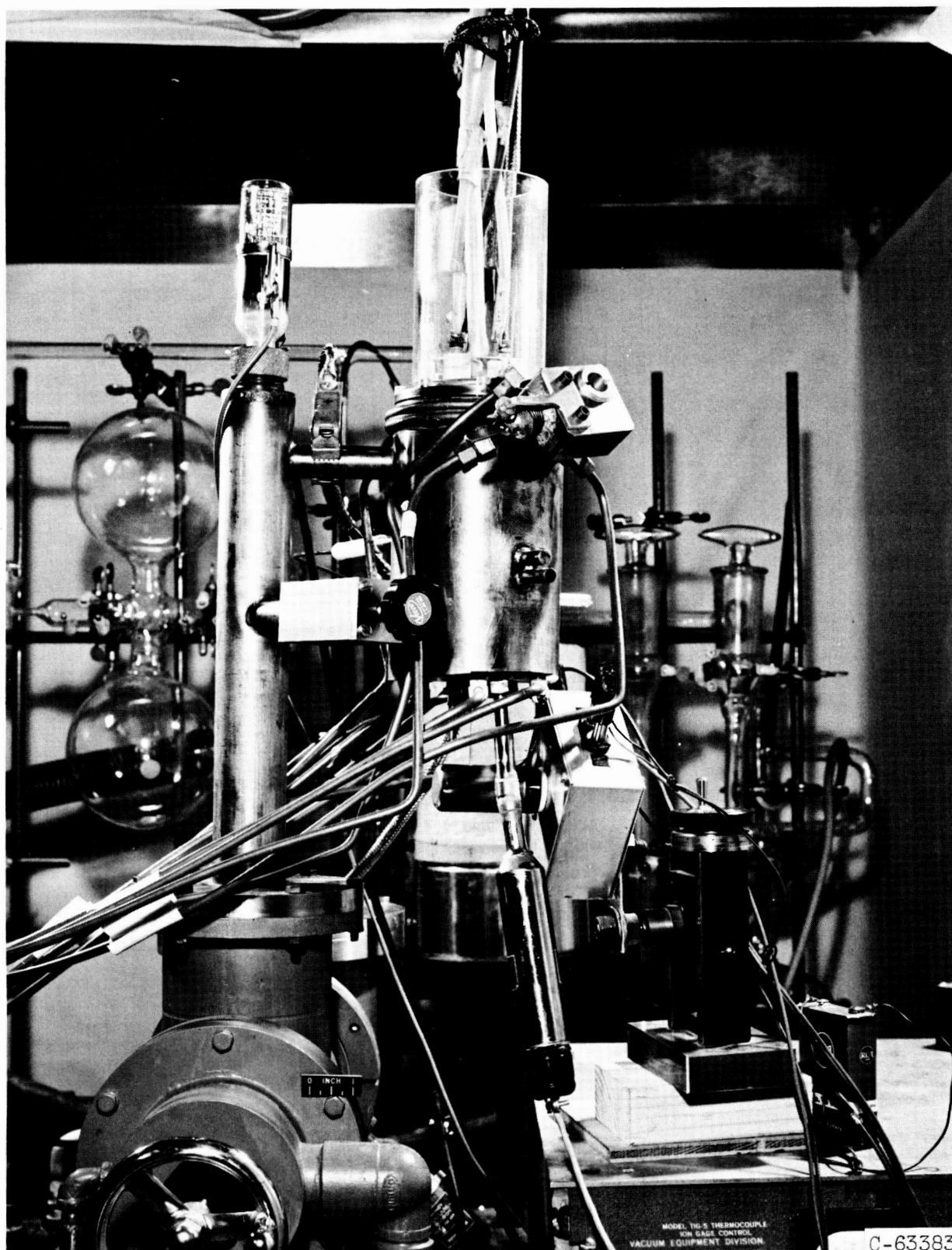


Figure 2. - Overall view of experimental apparatus.

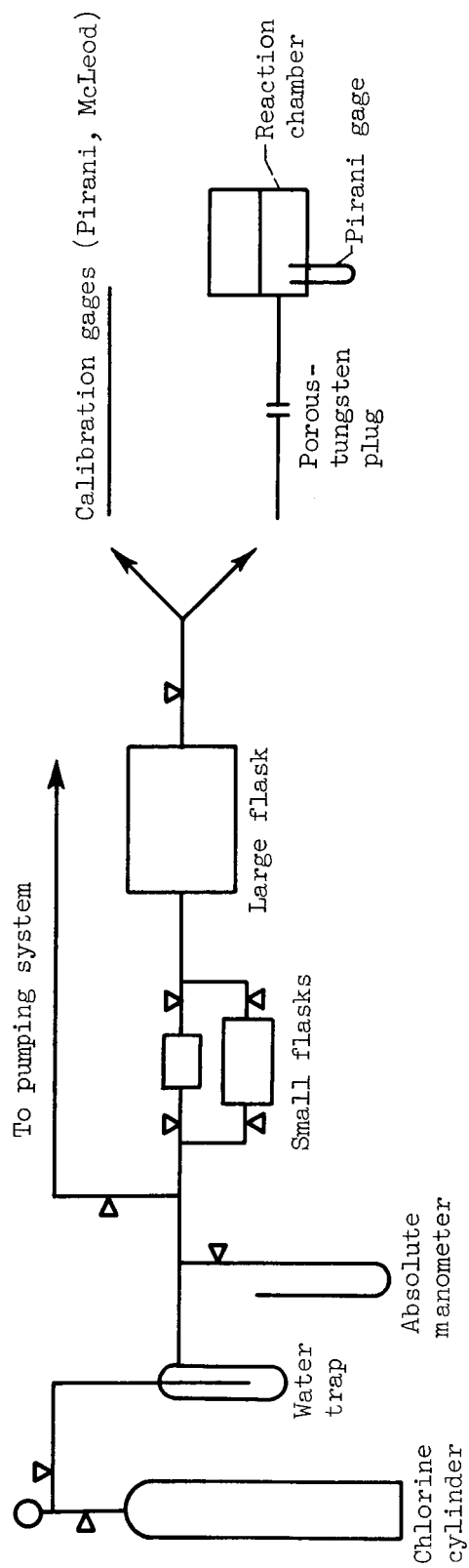


Figure 3. - Schematic drawing of gage-calibration and chlorine-metering system.

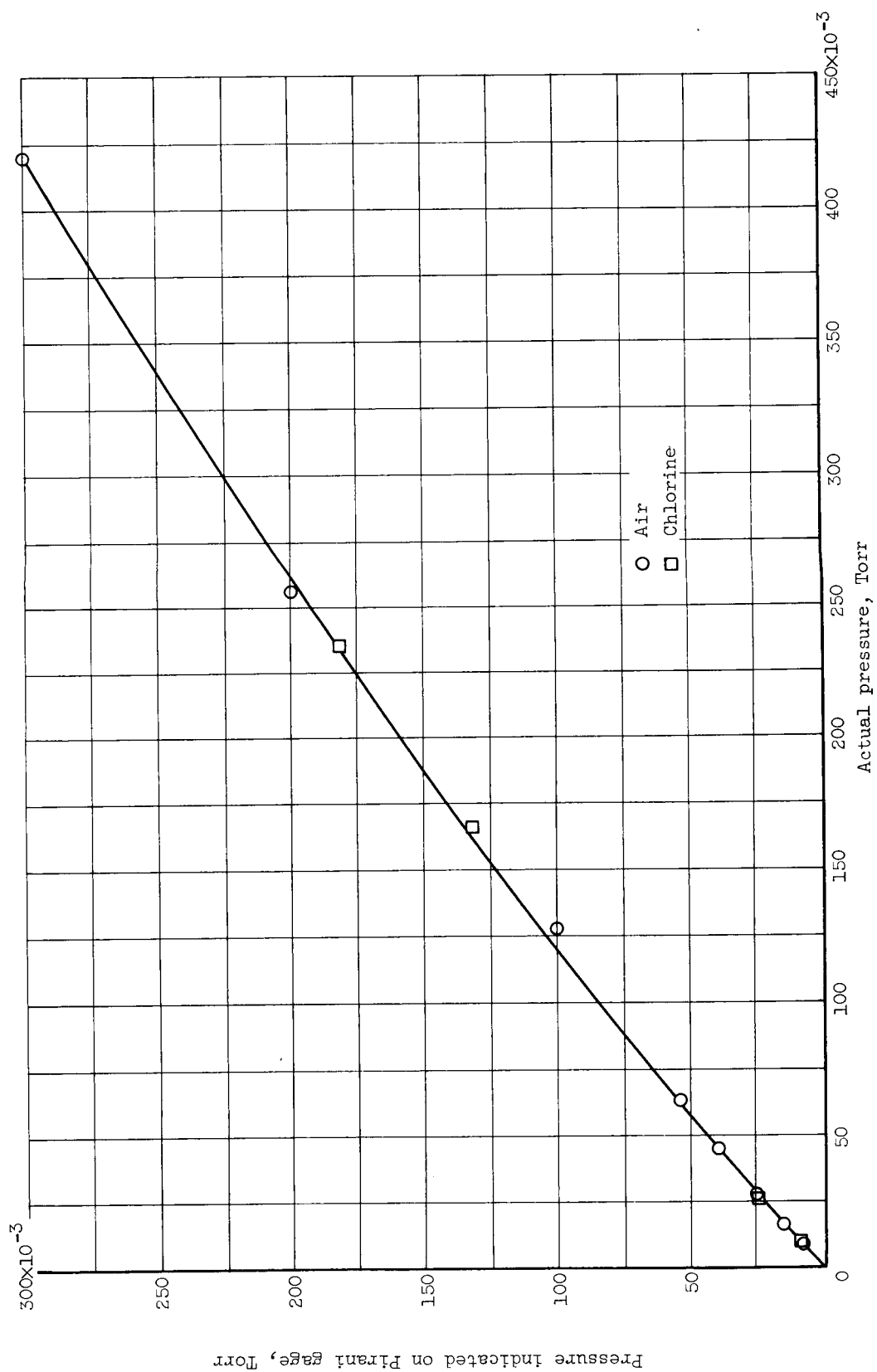


Figure 4. - Calibration of Pirani gage with air and chlorine. Actual pressure obtained from McLeod gage or by volume expansion method.

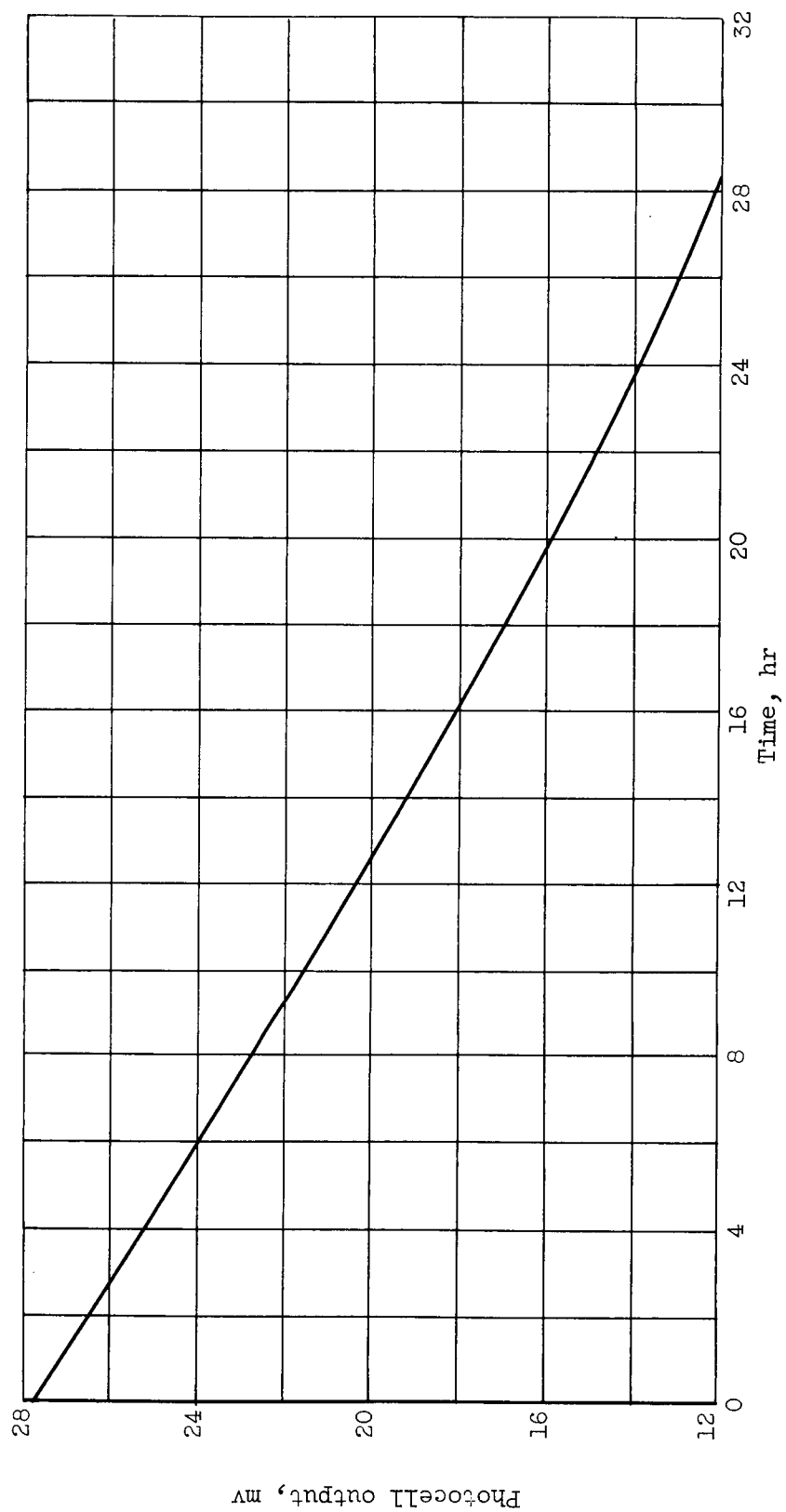
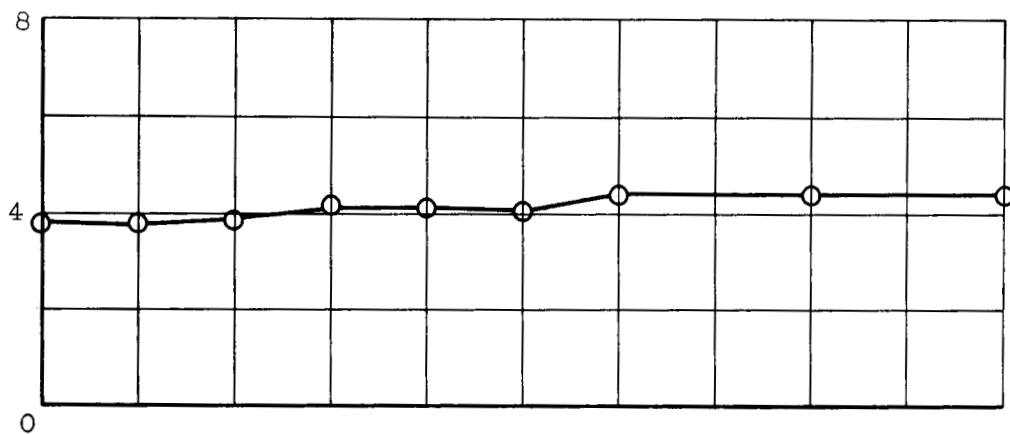
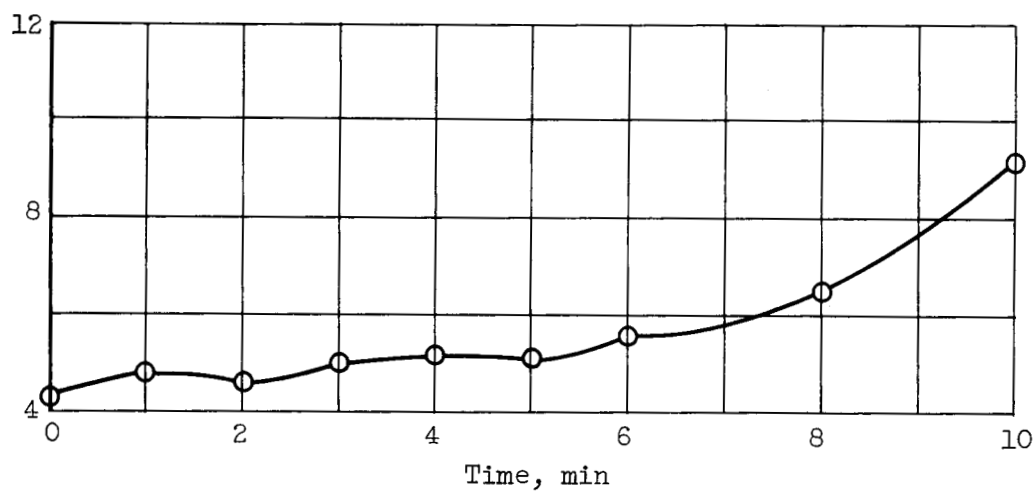


Figure 5. - Effect of condensing tungsten film on light transmission through sapphire rod. Emitter temperature, 2305° K; collector temperature, 1535° K.

Photocell output, mv

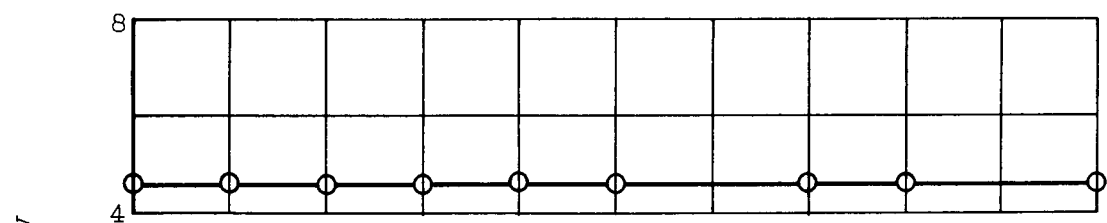


(a) Emitter temperature, 2173° K; collector temperature, 1472° K; chlorine pressure, 1.8×10^{-3} Torr.

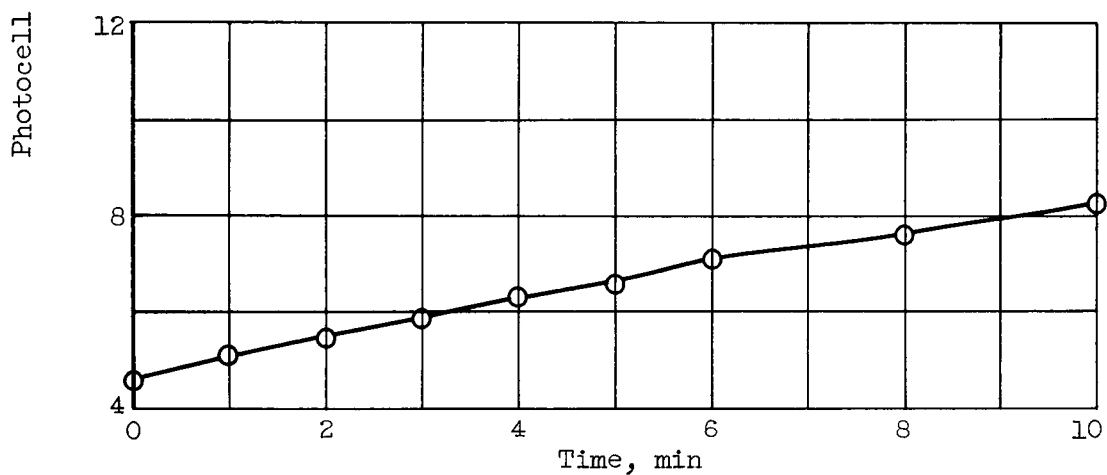


(b) Emitter temperature, 2173° K; collector temperature, 1472° K; chlorine pressure, 5.2×10^{-3} Torr.

Figure 6. - Variation of light transmission with time for chlorine pressures from 1.5×10^{-3} to 13×10^{-3} Torr.



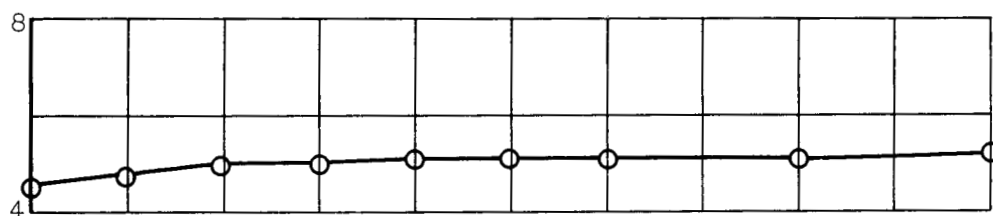
(c) Emitter temperature, 2347°K ; collector temperature, 1519°K ;
chlorine pressure, 1.8×10^{-3} Torr.



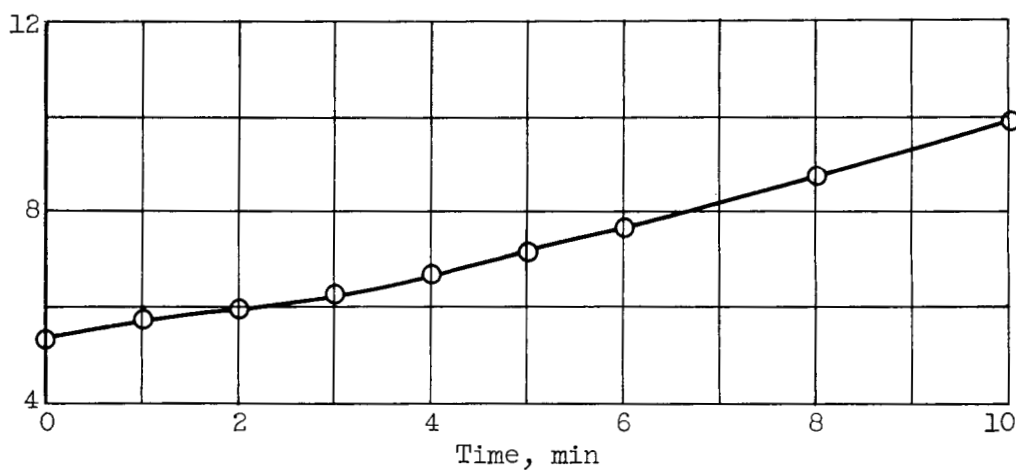
(d) Emitter temperature, 2347°K ; collector temperature, 1519°K ;
chlorine pressure, 9.3×10^{-3} Torr.

Figure 6. - Continued. Variation of light transmission with time for chlorine pressures from 1.5×10^{-3} to 13×10^{-3} Torr.

Photocell output, mv

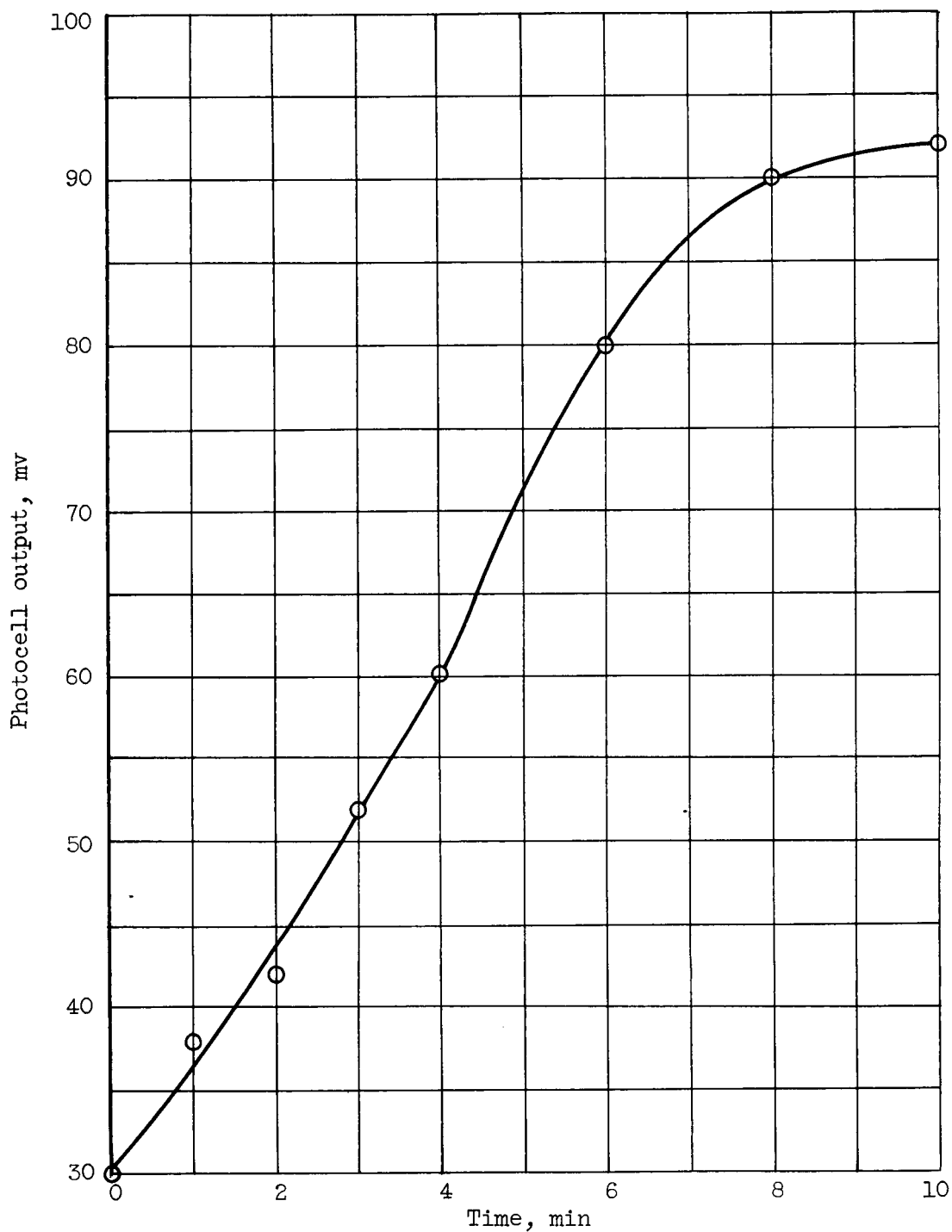


(e) Emitter temperature, 2413° K; collector temperature, 1478° K; chlorine pressure, 1.5×10^{-3} Torr.



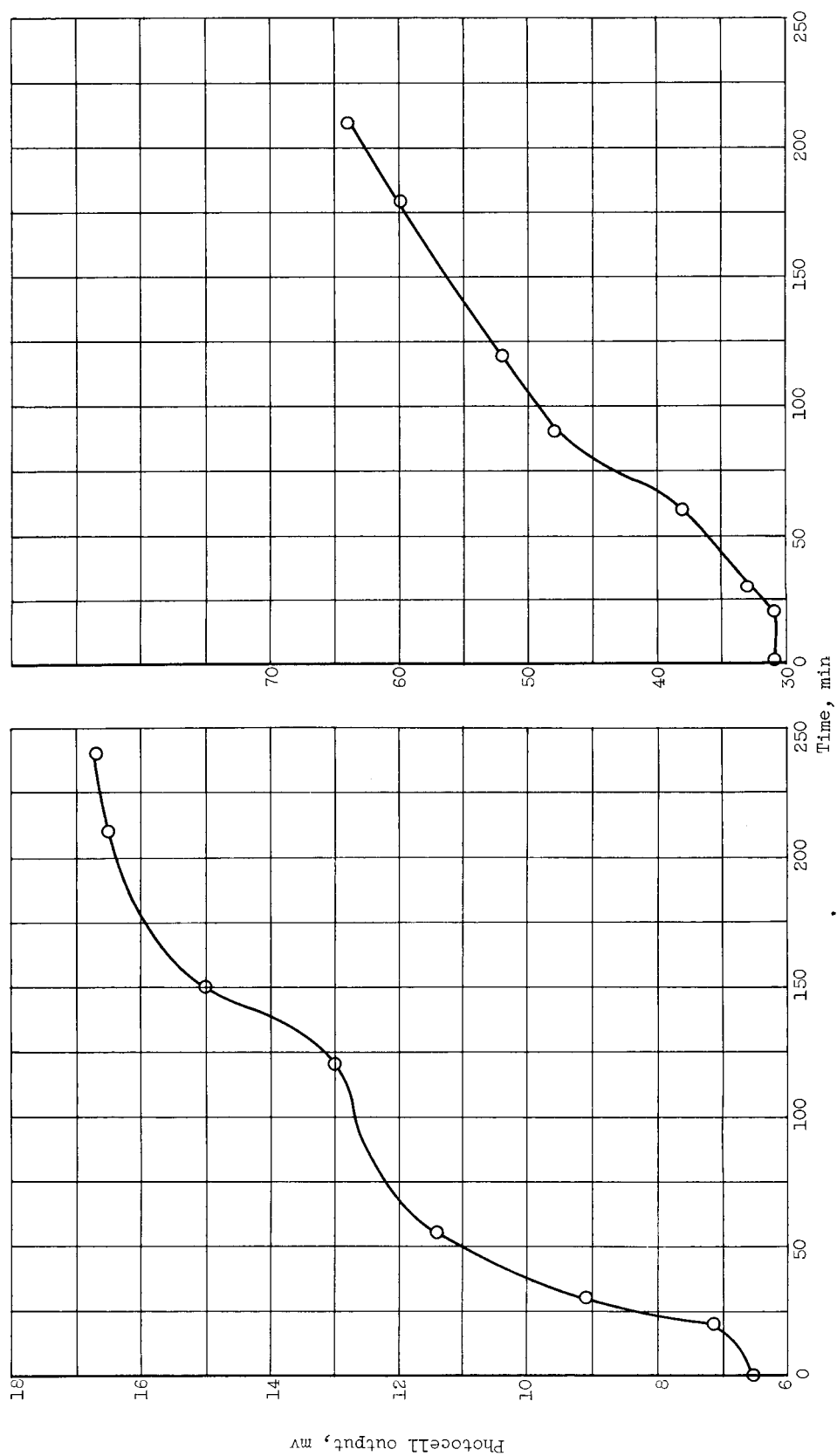
(f) Emitter temperature, 2413° K; collector temperature, 1478° K; chlorine pressure, 4.9×10^{-3} Torr.

Figure 6. - Continued. Variation of light transmission with time for chlorine pressures from 1.5×10^{-3} to 13×10^{-3} Torr.



(g) Emitter temperature, 2548° K; collector temperature, 1733° K;
chlorine pressure, 13×10^{-3} Torr.

Figure 6. - Concluded. Variation of light transmission with time
for chlorine pressures from 1.5×10^{-3} to 13×10^{-3} Torr.



(a) Emitter temperature, 2177°K ; collector temperature, 1461°K ; chlorine pressure, 0.4×10^{-3} Torr. (b) Emitter temperature, 2464°K ; collector temperature, 1680°K ; chlorine pressure, 2×10^{-3} Torr.

Figure 7. - Variation of light transmission with time for chlorine pressures of 0.4×10^{-3} and 2×10^{-3} Torr.

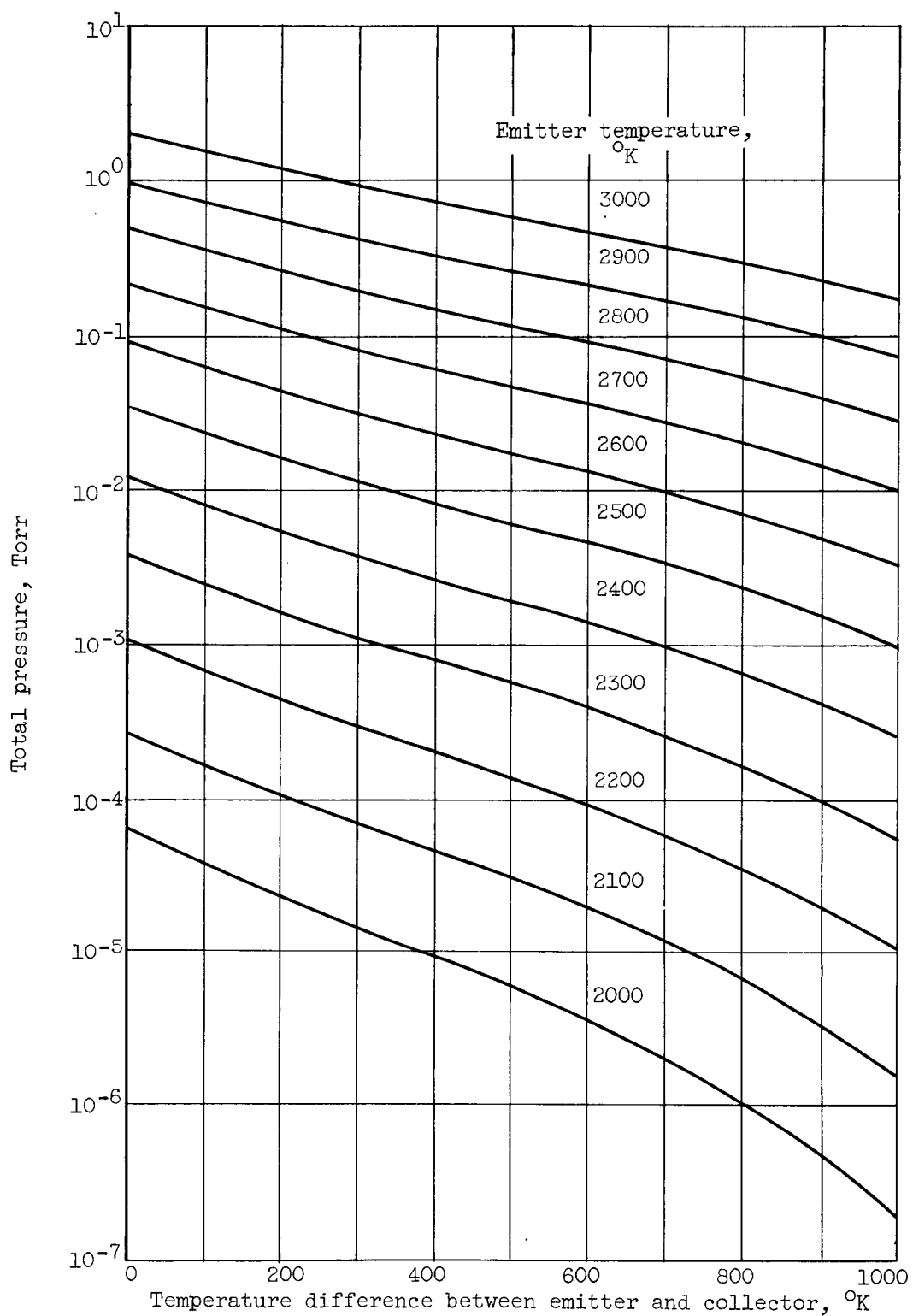
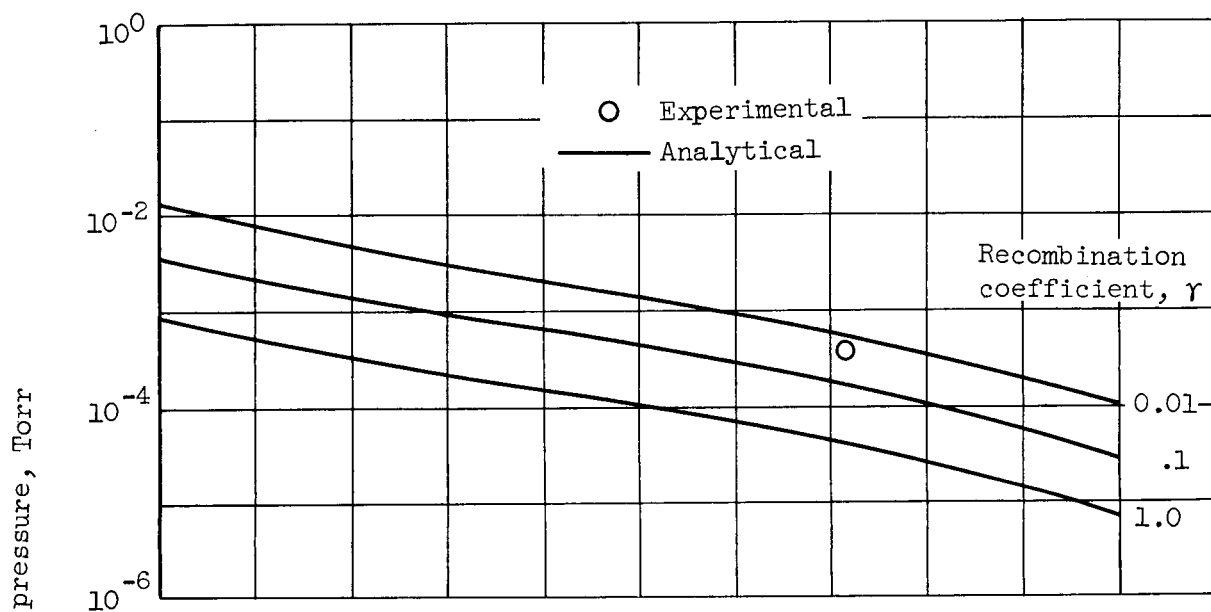
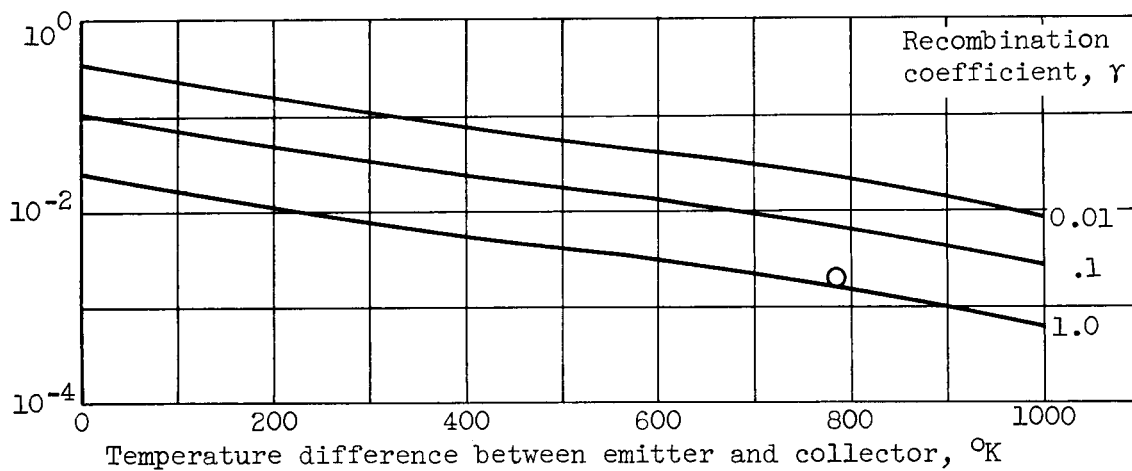


Figure 8. - Total pressure required for chemical regeneration under conditions of free-molecule flow in tungsten-chlorine system. Recombination coefficient, 1.0.



(a) Emitter temperature, 2177°K .



(b) Emitter temperature, 2464°K .

Figure 9. - Comparison of analytical and experimental data.